APPLIED ICME FOR NEW PROPULSION MATERIALS

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PM057

Overview

Timeline

- Project start date: Q4 FY13
- Project end date: Q4 FY17
- Percent complete 10%

Budget

- Total project funding
  100% DOE
- Funding received in FY13
  $70 K
- Funding for FY14
  $580 K projected budget
  ($280 K received to date).

Barriers

- Develop materials with lower **cost, time and risk** (ICME).
- Cost/limited supply of rare-earths for permanent magnets (EV & HEV).
- Durable low temperature catalysts for exhaust treatment.
- Piezoelectrics for high performance fuel injectors.
- High performance thermoelectrics for waste heat / climate control.

Partners

- John Deere, MIT (S3TEC EFRC), University of Tennessee, Critical Materials Institute, Naval Research Lab., Univ. of Houston.
- Project lead – ORNL.

ICME Applied Materials Discovery

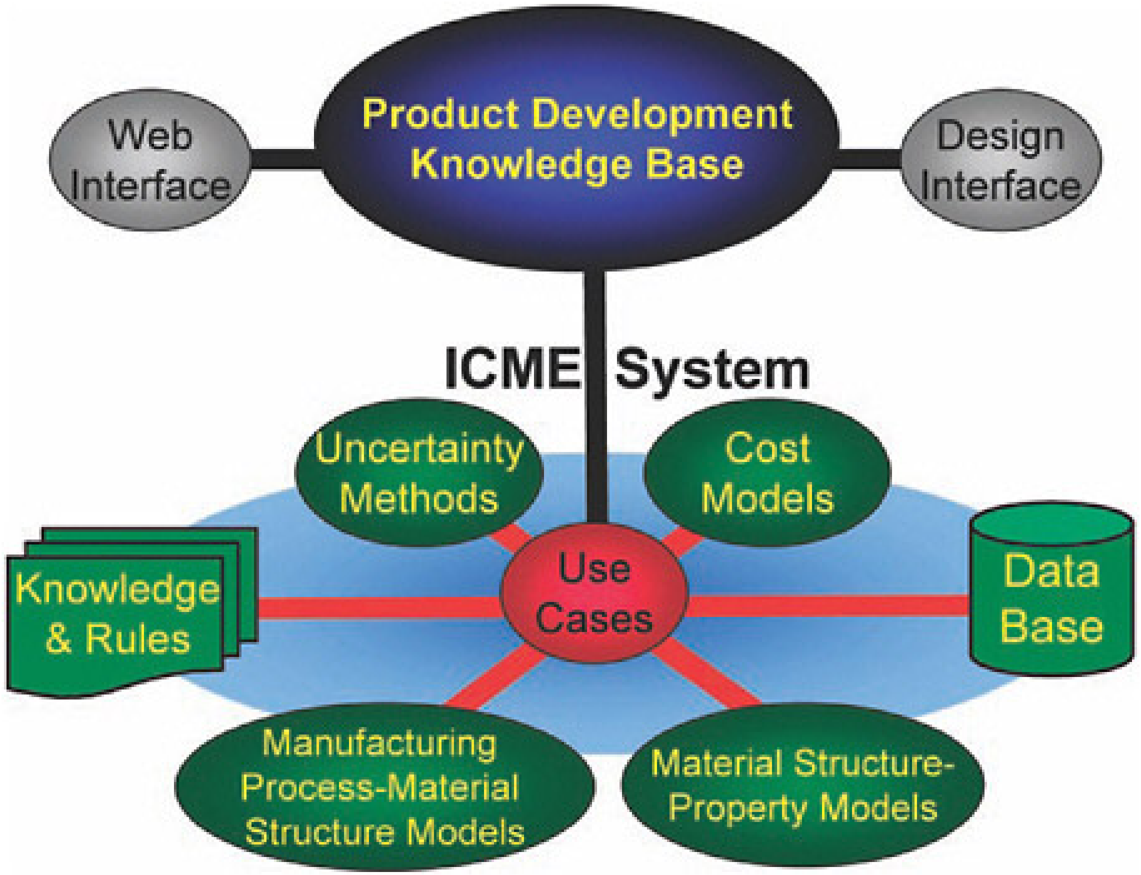
- Identify practical materials to reduce petroleum dependence by developing enabling materials.
- Develop/demonstrate applied ICME that can be used for practical propulsion materials development.
- New project: 4th quarter of FY13.

Applied ICME sub-projects	Project ID	Project PI	FY14 Budget
1. Piezoelectric materials	26391	D. Singh	$100,000
2. Thermoelectric materials*	26391	D. Parker	$50,000
3. Non rare earth permanent magnets*	26391	M. McGuire	$190,000
4. Catalyst materials*	26391	C. Narula	$190,000
			$580,000

**began work under a previous project*

Relevance: ICME

(Integrated Computational Materials Engineering)



Schematic structure of an ICME system from "Integrated Computational Materials Engineering, NAS Press (2008).

Driver (Barrier): Materials development is enabling for new technology, but is slow and expensive – need more efficient approaches (Materials Genome Initiative, OSTP).

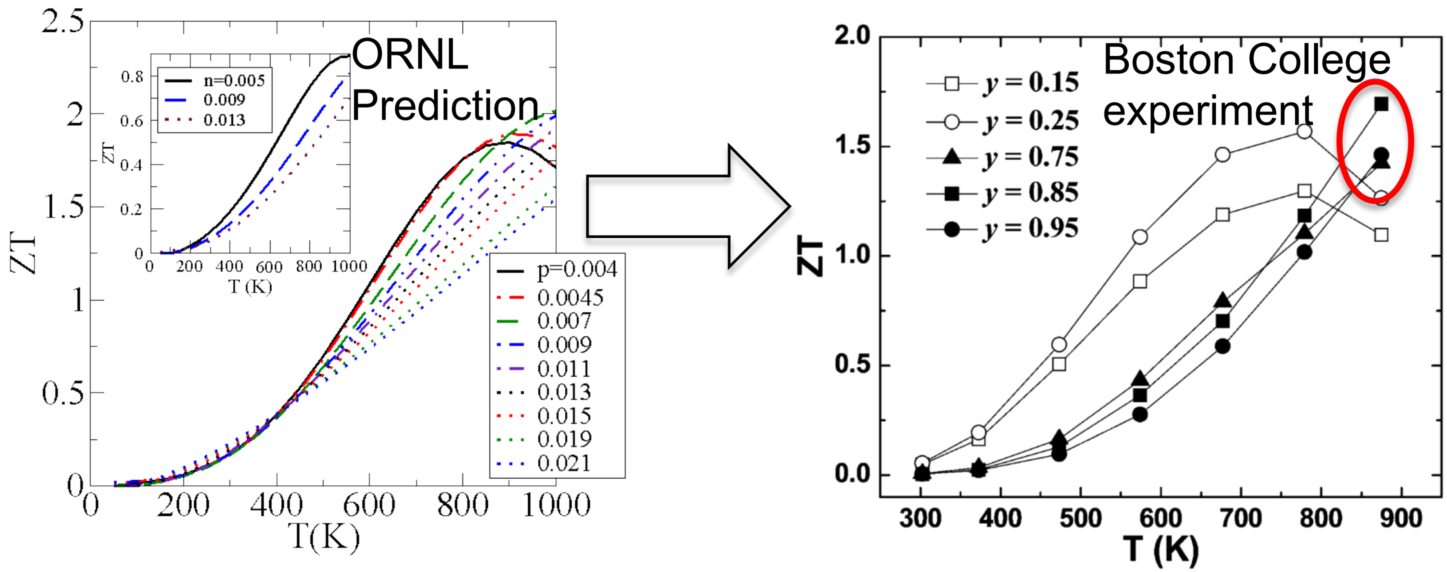
Depends strongly on the materials type and application.

Synergy and tighter coupling between activities (modeling, experiment) is a key ingredient.

Make materials development ***Faster, Cheaper and less Risky.***

ORNL Prediction and Confirmation (Thermoelectrics)

Goal is to identify high ZT thermoelectrics for waste heat recovery and climate control (EV enabler).



PbSe is lower cost than PbTe (Te free).

We predicted high p-type thermoelectric performance in PbSe[1] (ZT approaching 2); Confirmed by subsequent experiment[2]

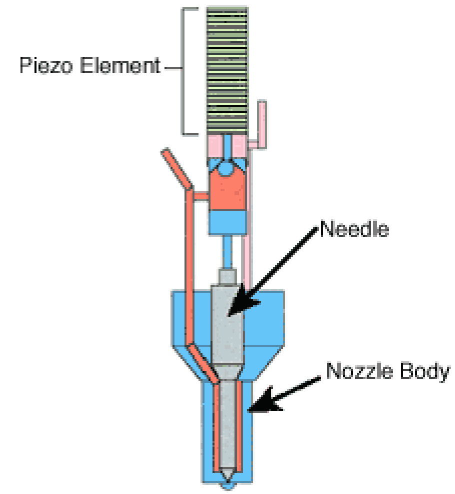
1. D. Parker and D.J. Singh, Phys. Rev. B **82**, 035204 (2010); 2. Q. Zhang, et al, J. Am. Chem. Soc. **134**, 10031 (2012).

Summary (Thermoelectrics sub-project)

- Relevance: Addresses materials for transportation (climate control and waste heat) and serves as an ICME demonstration with validation.
- Approach/Strategy: Perform first principles calculations to guide selection and optimization of thermoelectric materials.
- Accomplishments: Published technical reports on Mg_2Si, CoSbS and $CrSi_2$, low cost thermoelectric materials for use in exhaust waste heat recovery. Published technical report identifying acoustic impedance mismatch scattering as agent for thermal conductivity reduction in nanostructured thermoelectrics. Predicted high thermoelectric performance in PbSe. Patent granted on low cost skutterudite material.
- Collaborations: GM, Ford, MIT, Nav. Res. Lab., U. Wash., U. Houston.
- Proposed Future Work: Low cost thermoelectric materials potentially useful for room temperature heating/cooling applications and waste heat recovery. Demonstration of ICME approach.

Relevance: Piezoelectrics for High Performance Fuel Injectors

- Lack of adequate air-fuel control by current fuel management systems – needed for advanced combustion concepts to meet efficiency goals and EPA standards.*
- Fine dispersal and control of time profile of fuel injection are needed – done by using multiple opening and closings with precise durations and timing (multi-pulse injection; also ultra-high pressure direct injection).
- Need higher performance materials (displacement and authority).



Piezoelectric fuel injector – performance limited due to limitations on piezo-stack.

- Currently based on PZT ($PbZr_xTi_{1-x}O_3$).
- ***PZT was developed in the 1950's for SONAR transducers – not actuators.***
- Recent work (ORNL and elsewhere) suggests directions for improvement of PZT.

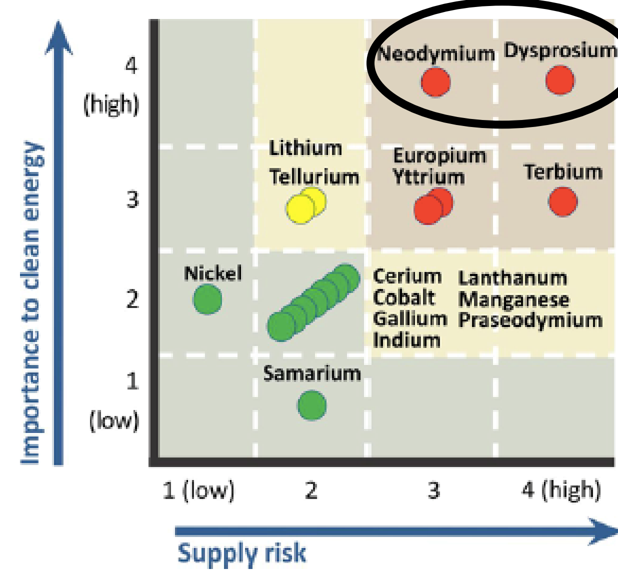
Driver is heavy duty vehicles, but advanced piezoelectrics will also benefit spark ignition engines for light duty and possibly natural gas.

* 21st Century Truck Partnership, "Roadmap and Technical White Papers", pp. 41-42, February 2013.

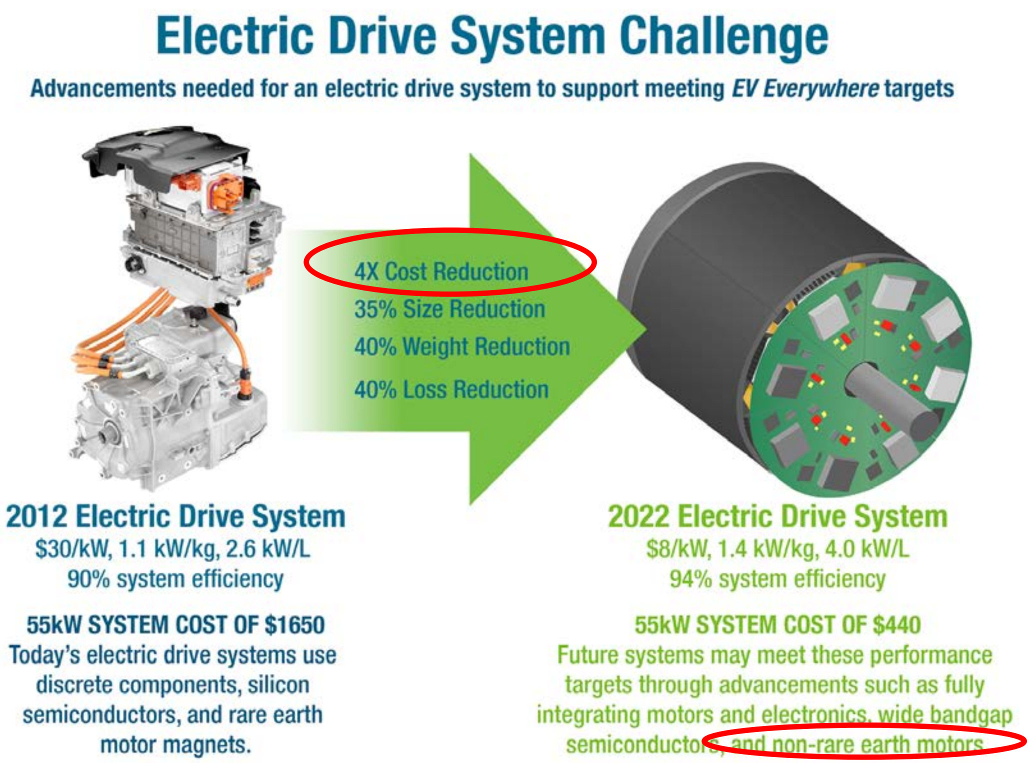
Relevance: Permanent Magnets

New high-performance, low-cost, motor magnets are needed to achieve EV Everywhere electric drive system cost and performance targets.

Eliminating rare earth elements will reduce cost and supply chain uncertainty.



DOE Critical Materials Strategy 2011



EV Everywhere Grand Challenge Blueprint (2013)

Rare earth permanent magnets account for:

- 40% of current motor materials cost.
- 30% of current motor cost.
- 60% of 2020 target motor cost.

DOE Vehicle Technologies Multi-Year Program Plan

Relevance: Catalyst Materials

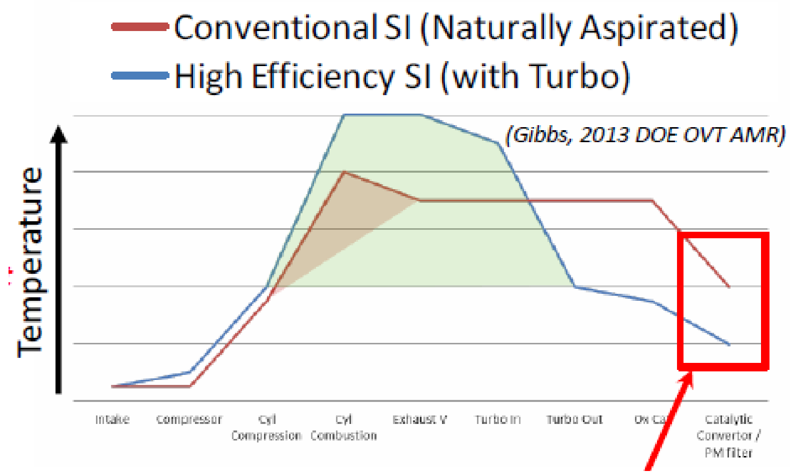
As advanced engines become more efficient, less heat energy goes into the exhaust

- Energy extracted by turbocharger.
- Lean burn lowers exhaust temperatures at light loads.
- High EGR levels lower exhaust temperatures.

→

Need low T performance to enable advanced engines that meet regulations (EPA Tier 3)

- Current catalysts for HC, CO, and NO_x are inadequate at low temperatures (~150°C).
- Must be stable at peak temperatures.



Lower catalyst temperatures

2013 CLEERS Industry priorities survey

USDRIVE "The 150°C Challenge" workshop report

2013 USDRIVE ACEC Tech Team Roadmap

Our Effort:

Supported clusters (Pt, Rh): oxidation and 3-way catalyst.

Urea-selective catalytic reduction (SCR): lean burn NO_x treatment technology (based on zeolites).

Milestones

DUE	Milestone	Status
Dec. 2013	(Thermoelectrics) Initial identification of a practical thermoelectric composition with theoretical performance equal to or better than commercial PbTe with no Te content based on electronic structure modeling.	Complete.
March 2014	(Thermoelectrics) Detailed modeling of a practical thermoelectric material with performance exceeding that of commercial PbTe but no Te content.	Complete (modified PbS compound for high T application, technical report).
June 2014	(Piezoelectrics) Identification of a practical oxide composition with a morphotropic phase boundary and an indicated polarization higher than that of PZT.	On track – finishing calculations to find location of MPB in PZT-Bi(Ti,Zn)O_3.
Oct. 2014	(Piezoelectrics) Identification of a practical oxide composition with a morphotropic phase boundary that has a larger lattice distortion than PZT as measured by the tetragonal c/a ratio on the tetragonal side of the boundary.	On track.
Oct. 2014	(Catalyst Materials) First principles studies of a supported catalyst to guide low-temperature catalytic activity.	On track.
Oct. 2014	(Catalyst Materials) Engine testing of heterobimetallic zeolite catalysts in collaboration with NTRC.	On track.
Oct. 2014	(Permanent Magnets) Identify one new rare earth-free ferromagnetic material composed of elements relevant for electric drive systems, and determine its potential for permanent magnet motor applications.	On track.

Approach: Piezoelectrics

Select likely modifications to PZT based on prior results, known trends, design rules.

FY13/14

Initial first principles exploration of properties of alloys near PZT.

Experiment: feasibility of synthesis and structural properties

FY14/15

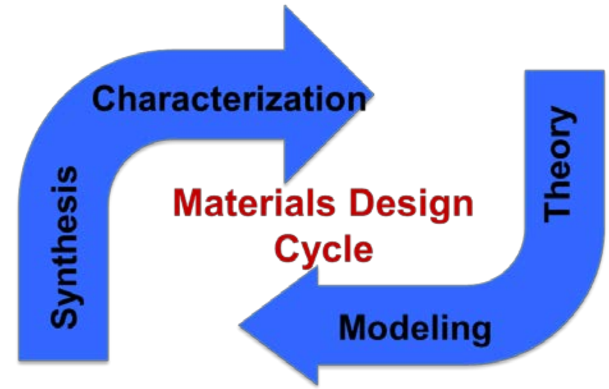
Selection of pseudoternary alloy system based on presence of MPB with high polarization/tetragonality

Detailed calculations: composition dependent properties.

Experiment: synthesis, ferroelectric characterization

FY15/16

Specific compositions and characterization of properties



ICME approach

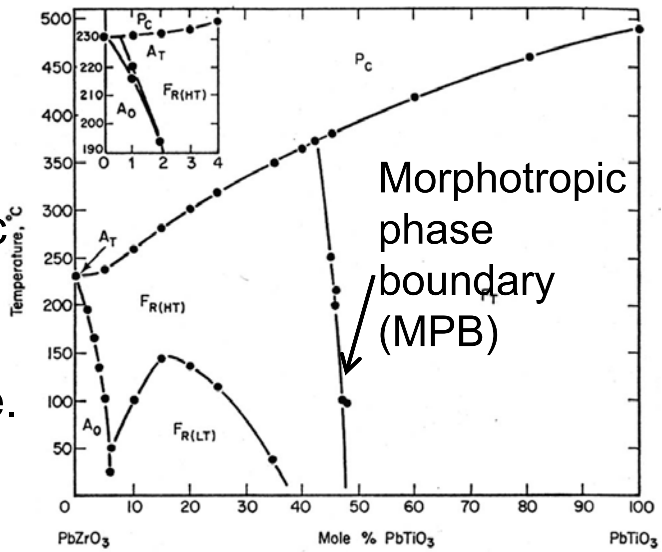
Continuous feedback between theory & experiment to accelerate materials development.

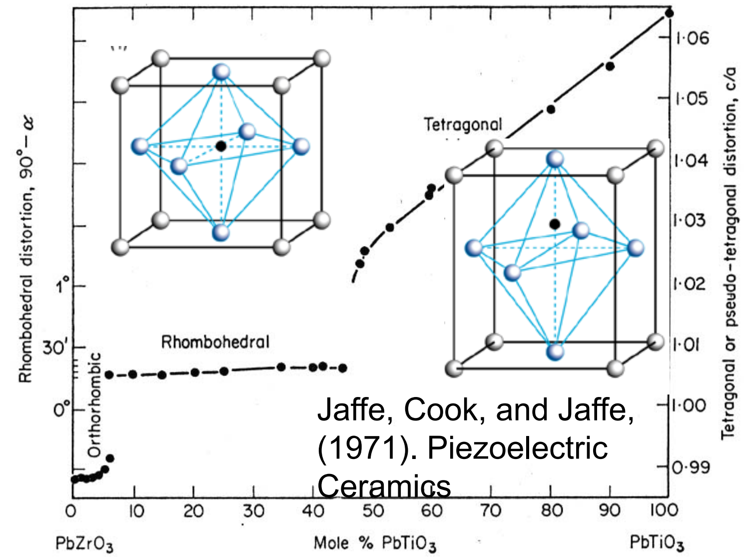
Technical reports will be published in order to make the results available to the community.

Example of Design Rules: Piezoelectrics

How PZT works:

Change of ferroelectric phase from tetragonal to rhombohedral at MPB ➔ high response.





Microscopic Parameters Controlling Performance:

- MPB (vs. phase separation).
- Tetragonality near MPB (c/a).
- Ferroelectric Polarization.
- Temperature dependence.
- Curie Temperature.
- Piezoelectric coefficients.
- Elastic properties.

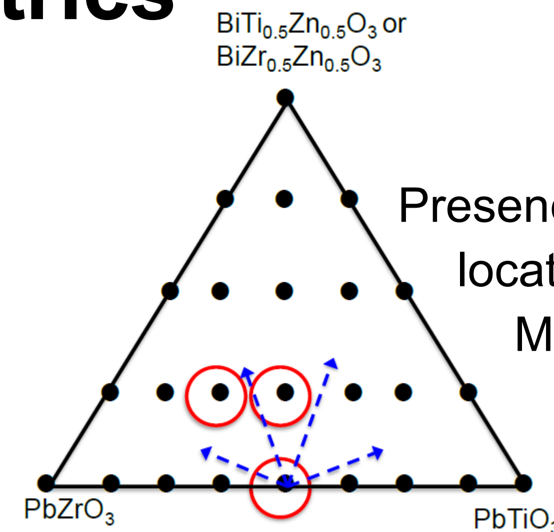
Chemical Trends/Knowledge:

- Lone pair physics vs. B-site (MPB).
- Bond-valence effect.
- Covalency and enhancement of Born charges.
- Competition of ferroelectric and tilt instabilities.
- A-site disorder effect (ORNL).

Accomplishments: Piezoelectrics

Selected two pseudoternary alloy systems to investigate based on “Design Rules”:

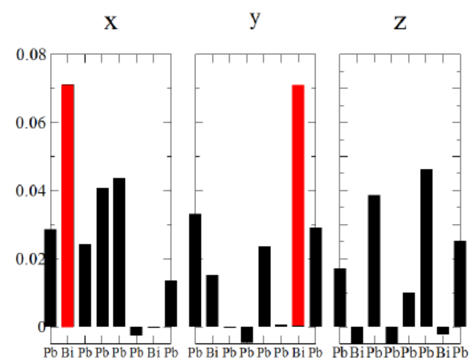
PZT – Bi(Ti,Zn)O_3 and PZT – Bi(Zr,Zn)O_3



Presence and location of MPB

Modelling: First principles supercell calculations for compositions near PZT – determining structure and atom off-centering:

- Position of MPB.
- Tetragonality.
- Ferroelectric polarization.

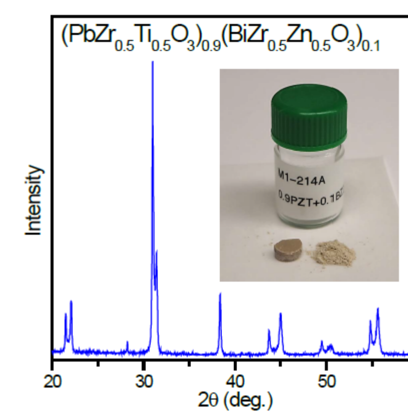


Enhanced A-site cation off-centering (polarization)

Experiment:

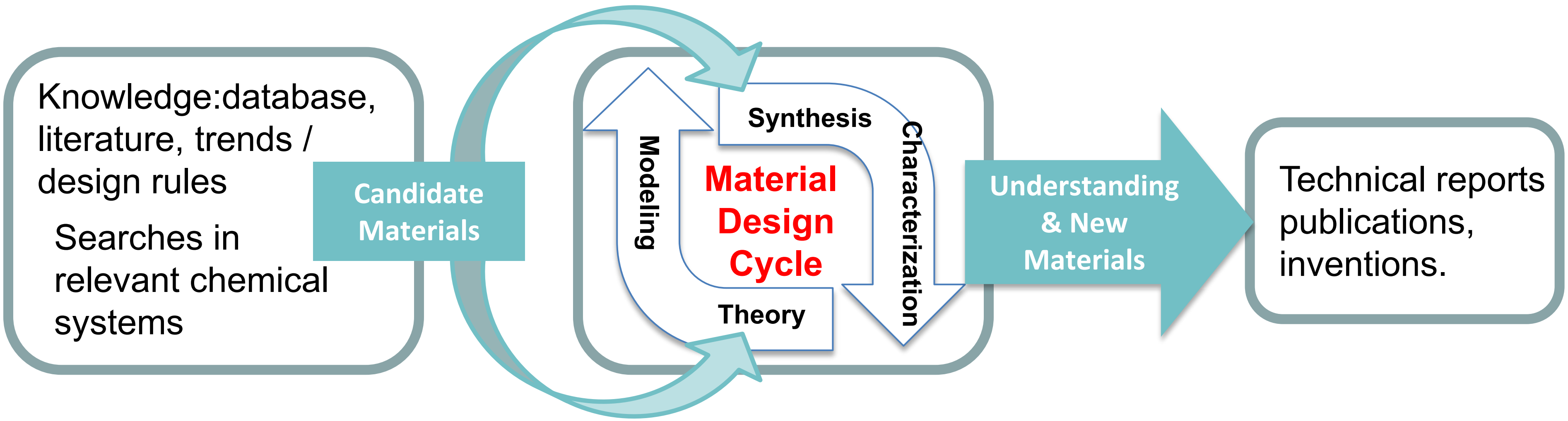
- Synthesis: Establish that the compositions can be readily made in practice
- Samples for structure determination.
- Feedback to theory.

Can be made by standard methods.



Approach: Applied ICME for Magnets

Use theory, modeling, materials synthesis, chemical tuning, characterization; take advantage of other unique capabilities and strengths at ORNL (processing, neutron scattering)



1. Starting point (chemical compound) is identified which meets certain requirements. *Potential high spin orbit, high magnetization, non-cubic structural environments.*

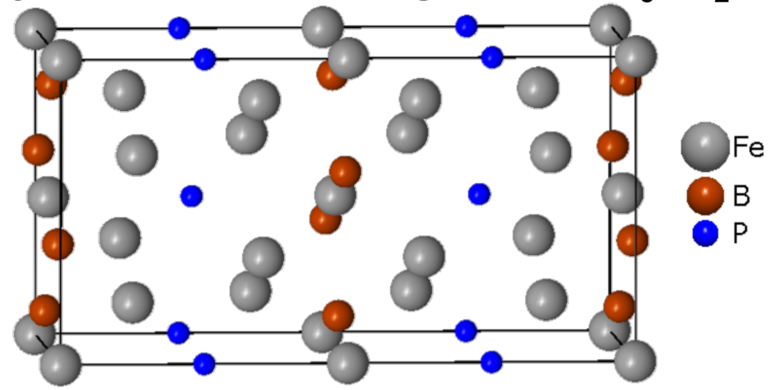
2. Understanding, optimization and manipulation of material properties using measurements / modeling modeling. *Most efficient with close coupling of theory and experiment*.

3. Findings reported and shared with community for specialized measurements, processing, prototyping, etc.

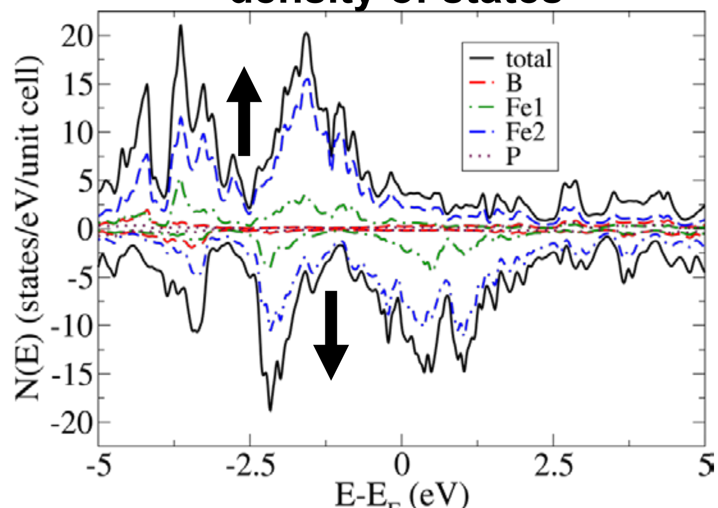
Accomplishment
Permanent Magnets

- Identified **Fe_5PB_2** as a promising and under-studied material with potential for permanent magnetic applications.
  - ferromagnetic
  - inexpensive components
  - high concentration of Fe
  - chemically flexible, uniaxial structure
- An extended family of related compounds
  - Fe_5PB_2 ferromagnet, T_C = 628 K
  - Fe_5SiB_2 ferromagnet, T_C = 784 K
  - Mn_5PB_2 ferromagnet, T_C = 312 K
  - Co_5PB_2, Mo_5PB_2, Nb_4SiB_2, W_5SiB_2…
- Effects of chemical substitutions on magnetism have been calculated.
- Synthesis efforts underway to examine the most promising directions indicated by theory.

Crystal structure tetragonal of Fe_5PB_2



Calculated spin-polarized density of states



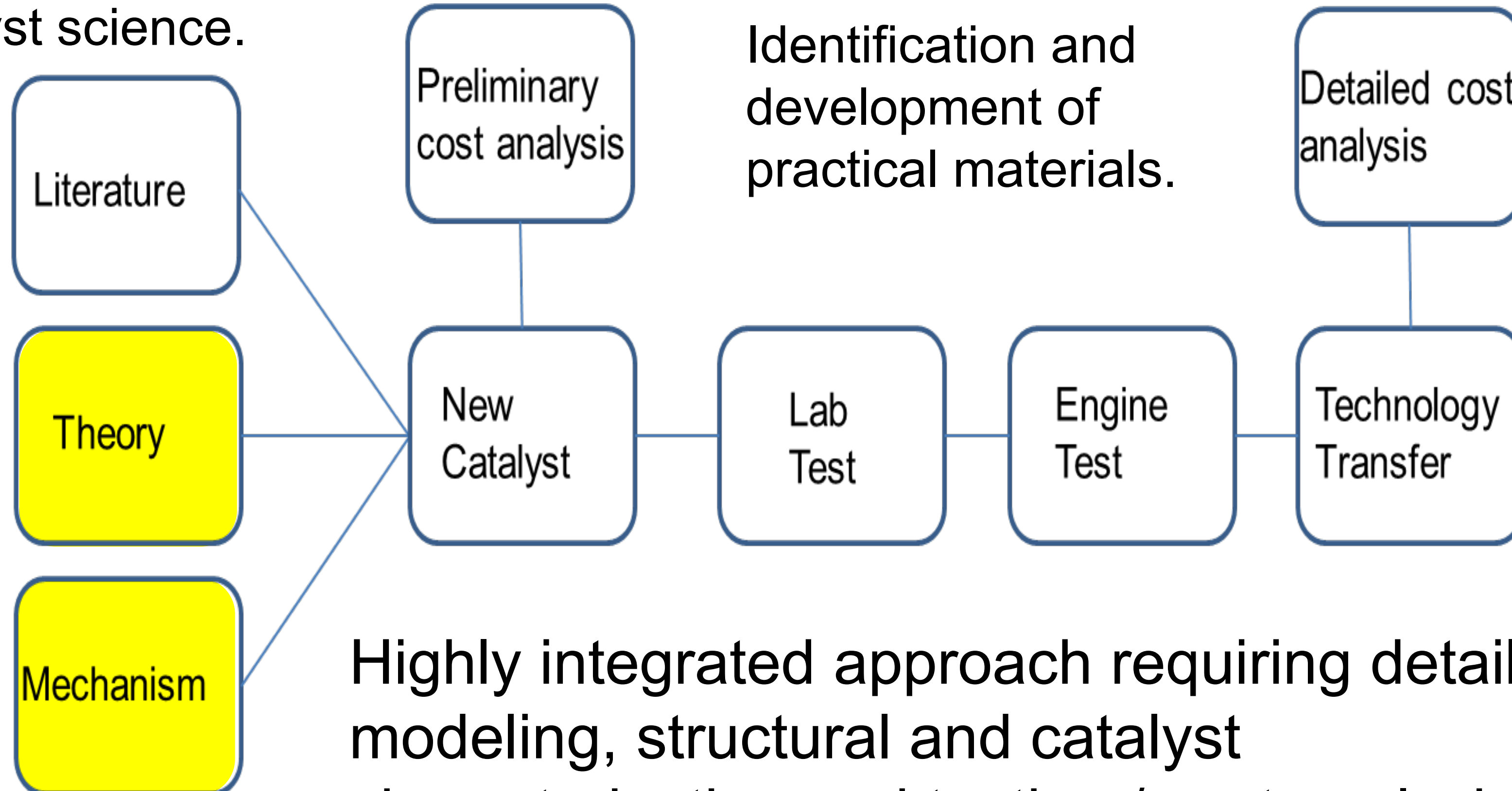
Fe_5PB_2 saturation magnetization

- calculated 1.32 T
- experimental* 1.28 T

* J. Solid State Chem. 13, 84 (1975).

Approach:
Applied ICME for Low-T Catalyst Materials

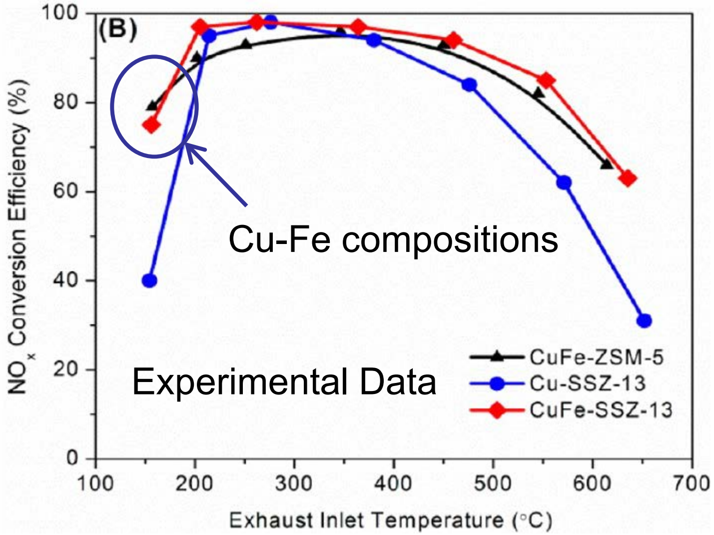
Theory, experiment, and characterization to rapidly advance catalyst science.

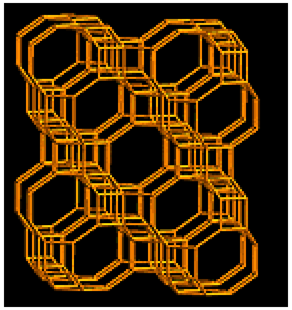


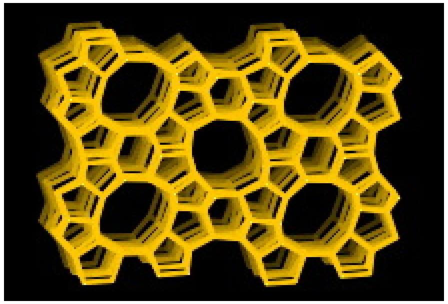
Identification and development of practical materials.

Highly integrated approach requiring detailed modeling, structural and catalyst characterization and testing / cost analysis, including engine testing.

Accomplishment: Heterobimetallic MFI Zeolite New Low Temperature NH_3 SCR Catalyst







Theory: iron exists as small oxide clusters Cu-SSZ-13 (left) and Cu-ZSM-5 (right) and is bonded to Cu via oxygen bridge. This arrangement enhances formation of NO+ ➔NO_x reduction.

- CuFe-SSZ-13 shows **remarkable low temperature reactivity** as compared with commercial Cu-SSZ-13 under **fast** SCR conditions
- CuFe-SSZ-13 is hydrothermally stable when tested after subjecting to accelerated aging protocol
- This year, we developed a simple impregnation route to prepare CuFe-SSZ-13 making it possible to fabricate fully functional catalyst on a honeycomb with little additional cost.
- Next Step – Develop and demonstrate catalysts for **standard** SCR.

Narula, C.K.; et al. J. Phys. Chem. 2012, 116, 23322

Responses to Prior Year Comments

New Project (No prior year comments).

Collaboration / Coordination with Other Institutions

- Massachusetts Institute of Technology (S3TEC Energy Frontier Research Center) – collaboration on thermoelectrics.
- Critical Materials Institute (DOE Hub), collaboration on magnets.
- John Deere – collaboration on catalysts NOX treatment.
- University of Tennessee – collaboration on magnetic materials, neutron scattering.
- University of Houston – collaboration on thermoelectrics.
- GM, Ford – discussions on thermoelectrics.
- Naval Research Laboratory – discussions on piezoelectrics.

Challenges and Barriers

New materials development is lengthy, costly and high risk:

Mitigate using ICME strategies.

Piezoelectrics: Need to quickly screen compositions – using averaging over moderate sized supercells; also using performance indicators.

Permanent Magnets: Rare earth elements provide intrinsic anisotropy to resist rotation of magnetization. Must use other heavy elements to get similar effects.

Permanent Magnets: Microstructure determines important aspects of magnetic performance (remanence, coercivity). Used melt-spinning to produce favorable microstructures in our Hf-Co-B alloys. Room for improvement here. Note that Intrinsic properties (saturation magnetization, magnetic anisotropy, Curie temperature) determine potential for good performance.

Catalysts: Large simulation cells and basis sets are needed for realistic modeling – developing collaboration for large scale molecular dynamics.

Catalysts: Bench top reactor throughput - have purchased MKS IR system which is being integrated to bench top reactor to enable faster catalyst testing.

Proposed Future Work

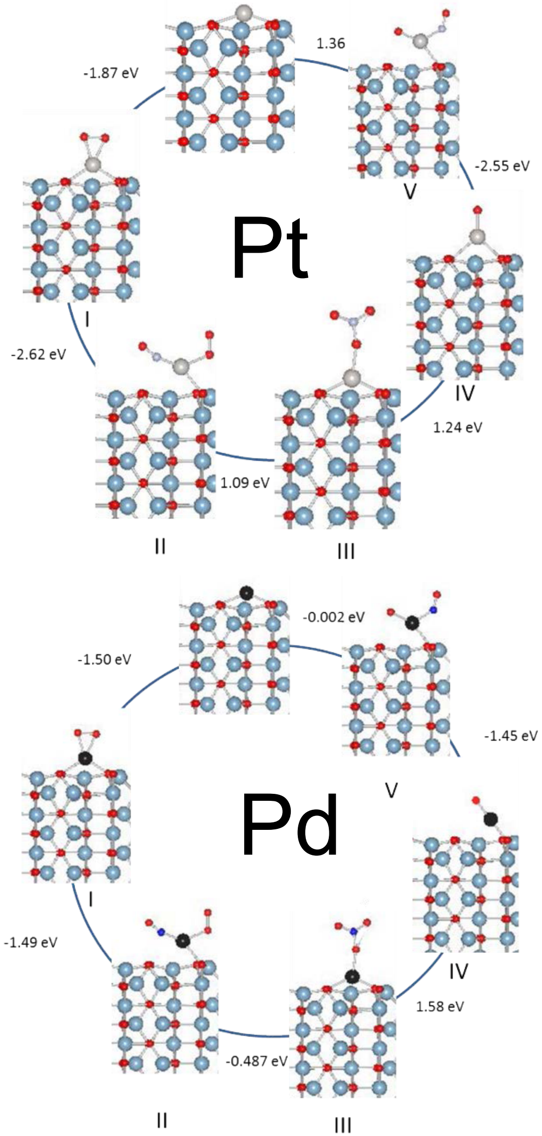
- **Piezoelectrics**: First principles calculations: identify materials with: large lattice distortion at the MPB for maximum actuation; large ferroelectric polarization; high ferroelectric Curie temperature. Continue focus on perovskite alloys related to PZT. Study the use of disorder to enhance properties – continue work on Bi-perovskite additions to PZT.
- **Permanent Magnets**: Improving $Hf_2Co_{11}B$-based alloys by chemical modification and crystallographic understanding, exploration of Cr/Mn/Fe/Co-rich phosphides for new ferromagnets, focus on Fe_5PB_2-type materials.
- **Catalysts**: First principles studies of supported catalyst to guide low-temperature catalytic activity – Complete NO oxidation study on single supported atoms – design of an effective low temperature NO oxidation catalyst.
- **Catalysts:** Engine testing of heterobimetallic zeolite catalysts in collaboration with NTRC - Results will validate laboratory scale observations under operating conditions.

Summary

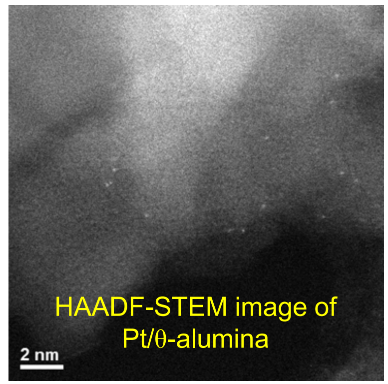
- **ICME Approaches to Address Materials Challenges.**
- Thermoelectrics for Waste Heat and Climate Control especially in EV.
- Piezoelectric Materials for High Performance Fuel Injectors.
  - fuel injectors relevant to advanced combustion engine development. Improved air-fuel control is needed for efficiency, emissions standards and customer acceptance (performance).
  - Selected materials systems for detailed study. Calculations imply of high polarization, possible morphotrophic phase boundary.
  - Experimental synthesis and characterization.
- Rare Earth Free Permanent Magnet Materials.
  - EV everywhere enabler. Addresses the cost and limited domestic supply of rare-earth elements, which are barriers to meeting motor cost targets and electrification.
  - Demonstrated melt-spun Hf-Co-B alloys as competitive rare-earth free permanent magnet materials with high Curie temperature (500 °C), energy products near 7 MGOe.
  - Identified Fe_5PB_2 as promising system for study in FY2014.
- Low Temperature Catalysts.
  - Enables fuel saving via lower exhaust temperature requirements.
  - Proposed single supported Pt atoms to be catalytically active based on models ➔ experimental evidence obtained with new mechanism supported by spectroscopic evidence..
  - Demonstrated low temperature NH3-SCR catalyst for fast SCR of Nox.

Technical Back-Up Slides

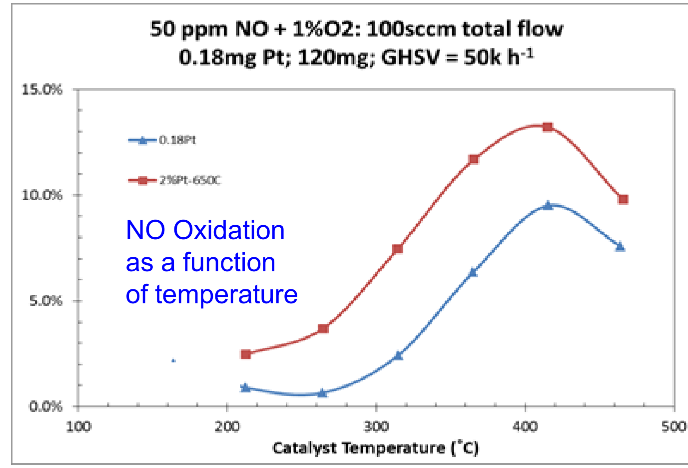
Progress: NO oxidation on single supported atoms



Proposed pathways for NO oxidation over single supported Pt and Pd



HAADF-STEM image of Pt/θ-alumina



NO Oxidation as a function of temperature

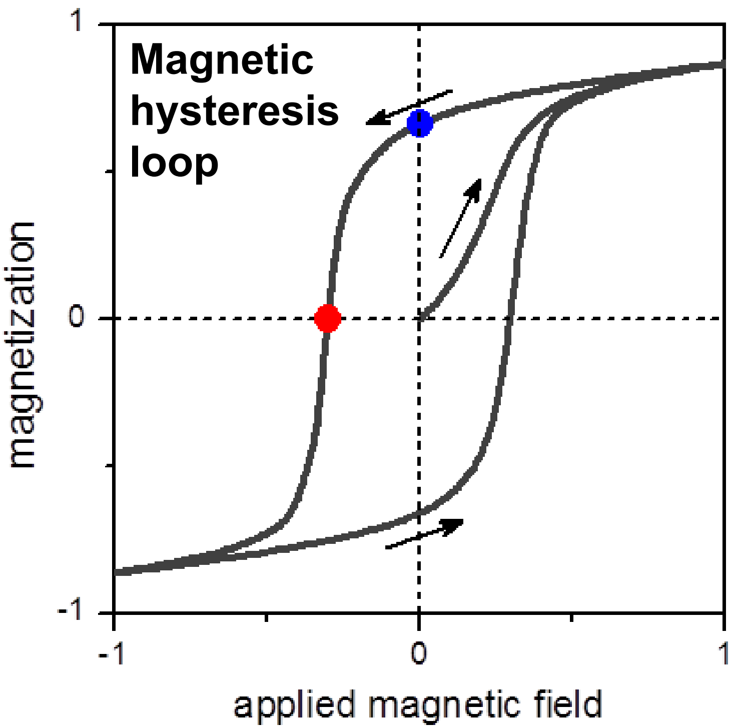
- Modelling: single supported atoms can be catalytically active [1] ➔ Synthesis / Characterization of mono-disperse single atoms on θ-alumina confirms for CO oxidation [2].
- Recent results: NO oxidation occurs on single supported Pt but requires high temperatures; more efficient on large particles – mechanism?
- Mechanistic studies suggest (1) no nitrate on Pt (2) nitrate on Pd at low temperature
  - DRIFTS should validate the mechanism

[1] Narula et al., J. Phys. Chem. **116**, 5628 (2012).
[2] Narula et al., JACS **135**, 12634 (2013).

Technical Background: Requirements for Good Permanent Magnets

Parameters characterizing magnetic performance:

- Curie temperature (T_C)
- Remanent magnetization (M_r), induction (B_r)
- Coercive field (H_c)
- **Energy product (BH)**



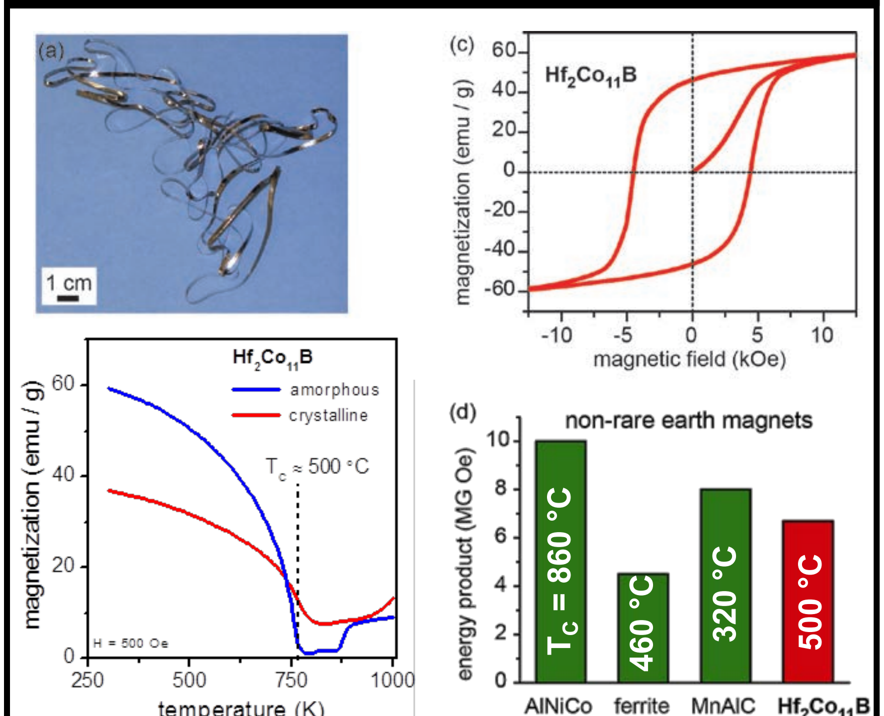
Material Requirements:

- **Large magnetic moments**: iron, cobalt (manganese, chromium)
- **One direction for magnetization**: non-cubic crystal structures
- **Co-alignment of magnetic particles**: highly textured microstructure
- **Strong resistance to switching magnetization direction (hard)**: *magnetocrystalline anisotropy*, small particles, refined microstructures
- **High Curie temperature**: strong magnetic interactions

Significant Accomplishment: $Hf_2Co_{11}B$ alloys

- **In previous project:** Identified $(Zr/Hf)_2Co_{11}$ as promising material for study.
- Modified composition with B and produced hard magnetic material directly via melt spinning.

$Hf_2Co_{11}B$: melt-spun ribbons and magnetic properties



- **Patent Application Filed Oct. 2013**

Key Findings:

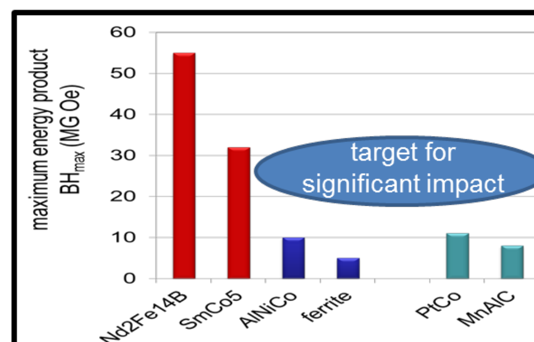
- **Demonstrated BH_{max} = 6.7 MGOe**

•Energy product competitive with well-established, long-studied non-rare earth magnet materials.

•Energy product near half that obtained in optimized NdFeB melt-spun ribbons.

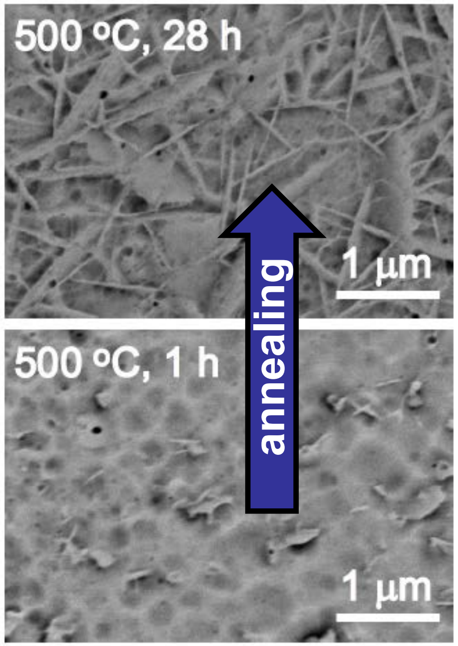
•Curie temperature ~150°C higher than NdFeB.

•*Analysis suggest at least a factor of two increase in energy product possible.*

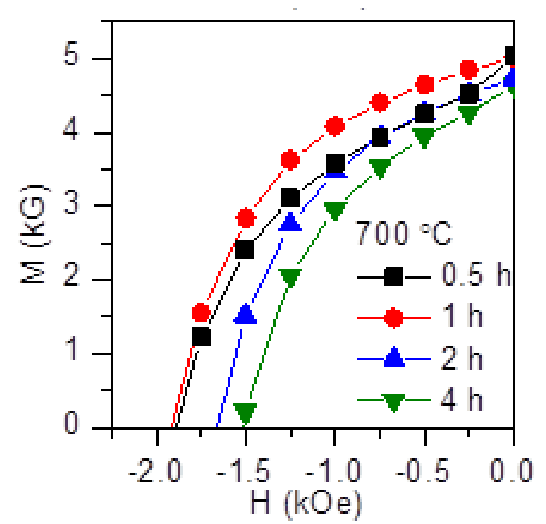


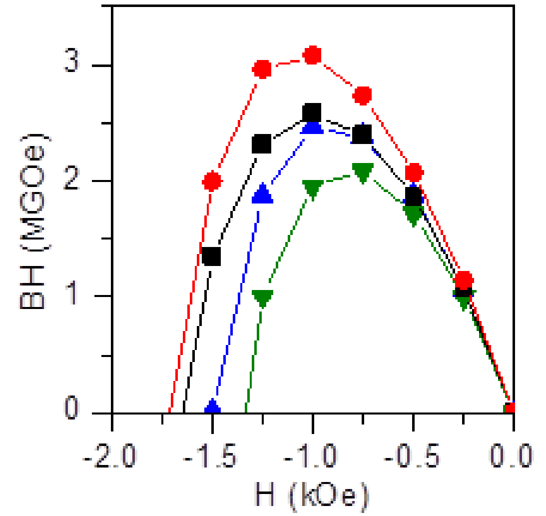
Recent Results: Development of Hard Magnetism by thermal treatment of amorphous $Hf_2Co_{11}B$

- **Goal: Develop hard magnetic behavior via annealing of amorphous precursor, and obtain information about the hard magnetic phase.**



- Extensive annealing study.
- Focus on microstructural evolution and development of magnetic properties.
- **Multiphase materials**
- Best properties obtained by processing far from equilibrium.





- Hard phase forms elongated precipitates.
- Coexistence with magnetically soft matrix gives best properties.
- Morphological identification of the hard phase enables *study of crystal structure and composition*.